

Recent Advances in Thermoplastic Puncture-Healing Polymers

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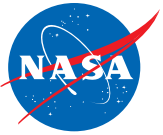


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AIAA Infotech@Aerospace 2010 in
Buckhead, GA

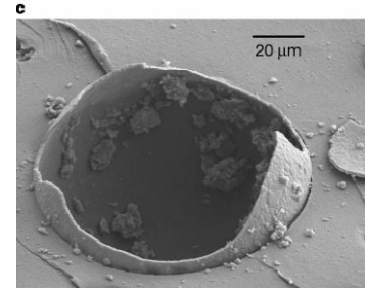
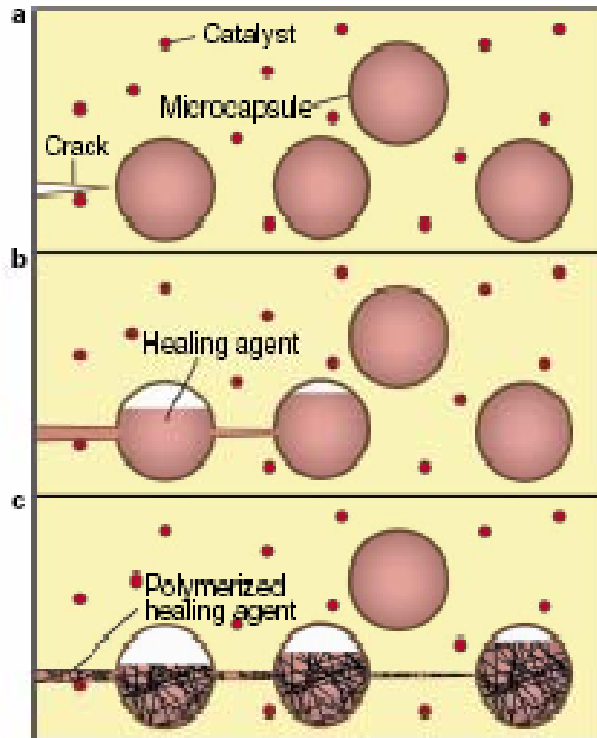
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Background Self-Healing Polymeric Materials

Autonomic Self healing of Polymeric Composites University of Illinois



Advantages

- Fast polymerization of DCPD
- Inexpensive DCPD
- Recovery of 60-90% of initial fracture load

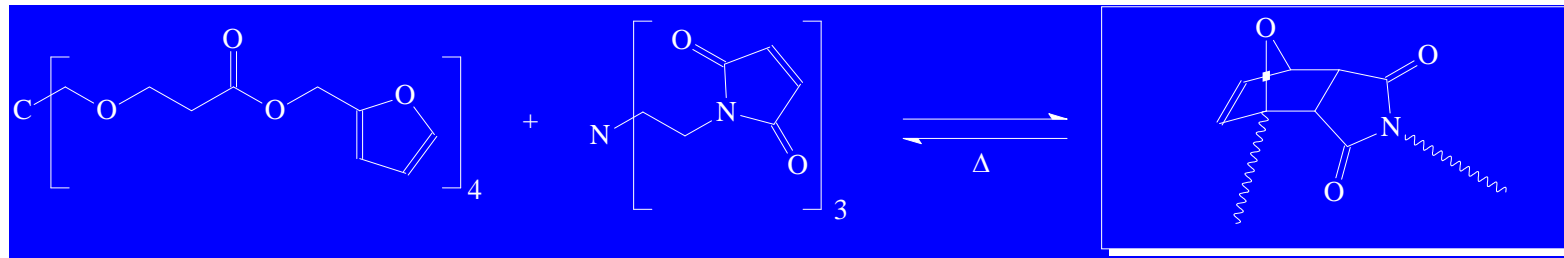
Disadvantages

- High cost of catalyst
- Amount of catalyst
- Stability of catalyst?
- Healing of crack along previous crack?
- Capsules may have detrimental effects on composite performance.

S.R. White, N.R. Sottos, J. Moore, P. Geubelle, M. Kessler, E. Brown, S. Suresh, S. Viswanathan, *Nature*, **409**, 2001, pp. 794-797.



Background Self-Healing Polymeric Materials



Advantages

- Easy and fast polymer synthesis
- Transparent material
- Retro-Diels-Alder reaction allows for remending of sample

Disadvantages

- Crack initiation led to fracture of sample---could not stop crack propagation
- Samples had to be held in intimate contact at high temperature for several hours for sample to remend
- A maximum of 50% of initial fracture load could be recovered
- Subsequent cracks propagate along original crack plane, with additional cracking adjacent to this crack

X. Chen, *et al.*, *Science*, **295**, 1698 (2002).

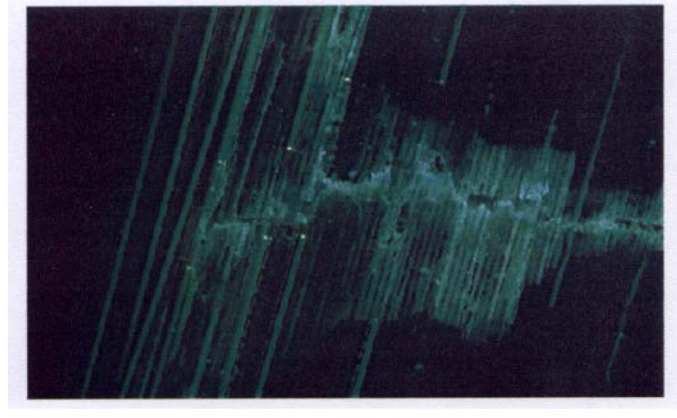
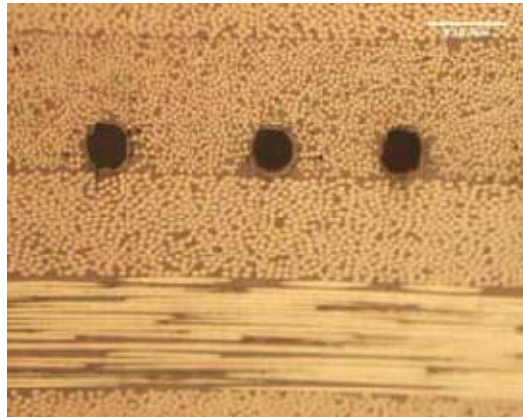
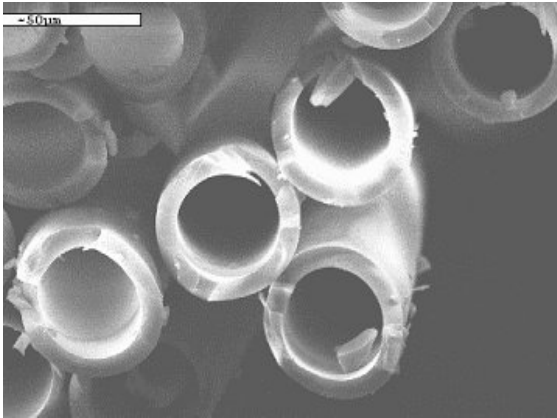


Background

Self-Healing Polymeric Materials

Brittle glass fiber reinforced plastics containing hollow fibers filled with epoxy hardener and uncured resin in alternate layers, with fluorescent dye

University of Bristol



- (a) *Hollow glass fibres, (b) Hollow glass fibres embedded in carbon fiber reinforced composite laminate, (c) Damage visual enhancement in composite laminate by the bleeding action of a fluorescent dye from hollow glass fibres*

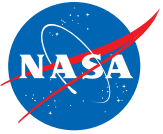
I. Bond and co-workers, *Composites A*, 32, (2001), 1767-1776.

Hucker MJ, Bond I, Bleay S, Haq S., *Composites A*, 34(11), (2003), 1045-1052



Puncture Healing Materials





Motivation

- Develop self-healing polymeric materials to enable damage tolerant systems.
 - Tailor puncture healing for use temperatures and applications.
- Benefit in environments and conditions where access for manual repair is limited or impossible, or where damage may not be detected.

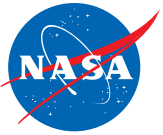


Approach

- Survey commercially available materials capable of puncture self healing.
- Determine puncture healing mechanism.
- Understanding guides design of range of new puncture self-healing materials.



Ballistics testing assembly



Methods

- Thermal and mechanical analysis of polymers
- Mid-velocity projectile tests on various commercially available polymers at various temperatures
- Measured initial and final bullet velocities with chronographs
- Measured site of impact temperatures with thermal imaging cameras
- Dynamic Mechanical Analysis
Time Temperature Superposition (TTS) master curve.
- High speed video

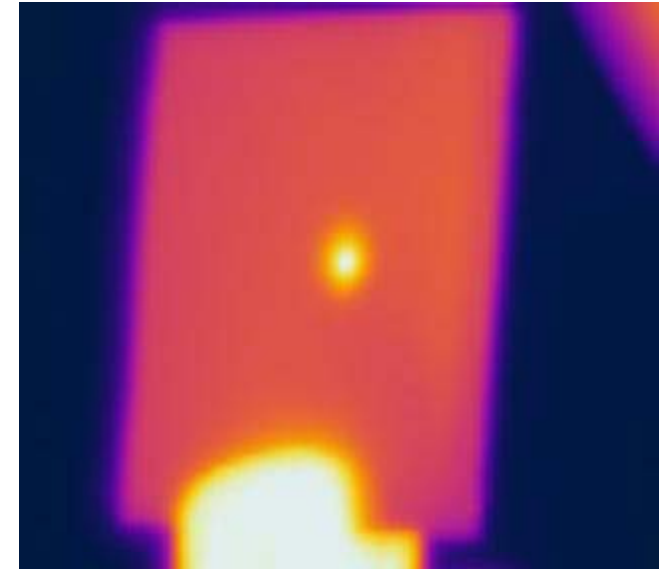


Ballistics testing assembly



Puncture Self-Healing Concept Background

- Puncture healing in these materials is dependent on how the combination of the polymer's viscoelastic properties responds to the energy input from the puncture event which results in an increase of temperature in the vicinity of the impact
- Self-healing behavior occurs upon projectile puncture whereby energy is transferred to the material during impact both elastically and inelastically thus establishing two requirements for puncture healing to occur:
 - (1) The need for the puncture event to produce a local melt state in the polymer material and
 - (2) The molten material has to have sufficient melt elasticity to snap back and close the hole



Thermal image of self healing panel immediately after projectile penetration

- Fall, R., Ward, T.C., *Puncture Reversal of Ethylene Ionomers-Mechanistic Studies*, Thesis, VA. Tech, 2001.
- Kalista, S.J., Ward, T.C., *Self-healing of Thermoplastic PEMAA copolymers Following Projectile Puncture*, Thesis, VA Tech, 2003.

Collaboration with Emilie Siochi with NASA-Langley Research Center



Thermal and Mechanical Property Characterization Results

Polymer	T _g (° C)	T _m (° C)	Elongation (%)	Tensile Strength (MPa)	Tensile Modulus (MPa)
Surlyn	-100	54,95	309	27.2	308.5
Affinity EG 8200	-68	46,66	947	9.3	5.9
PB-g-PMA-co-PAN	85	-	7.5	37.3	2472.5
Lexan	150	-	2.0	59.0	2900
PBT	70	210	250	50.0	2000
PBT-co-PAGT	66	180	500	6.9	188



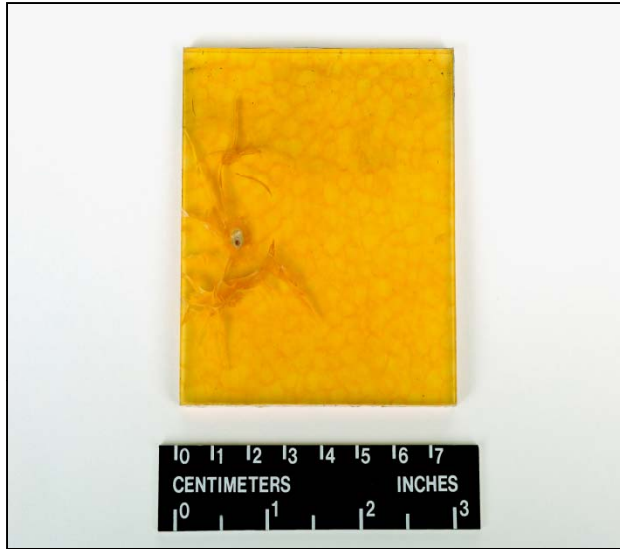
Ballistic Testing Results

Polymer	Test Temp (° C)	Site of Impact Temp (T _i) (°C)	T _g (° C)	T _m (° C)	Hole Diameter (mm)	Self healing (Y or N)
Surlyn	25	127	-100	54,95	--	Y
Affinity EG 8200	25	77	-68	46,66	--	Y
PB-g-PMA-co-PAN	25	133	85	-	.5	N
	50	127			--	Y
Lexan	25	--	150	-	--	N
	100				4.0	N
PBT	25	--	70	210	--	N
	100				3.0	N
PBT-co-PAGT	28	--	66	180	--	N
	100				1.0	N

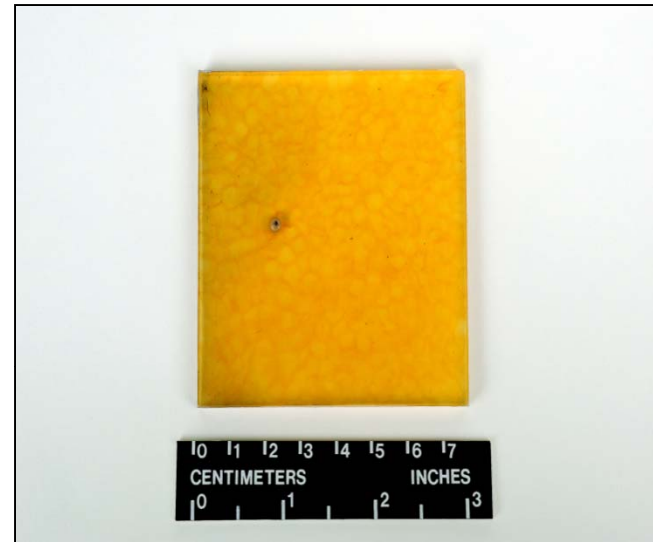


Ballistic Testing Results

(PB-g-PMA-co-PAN)

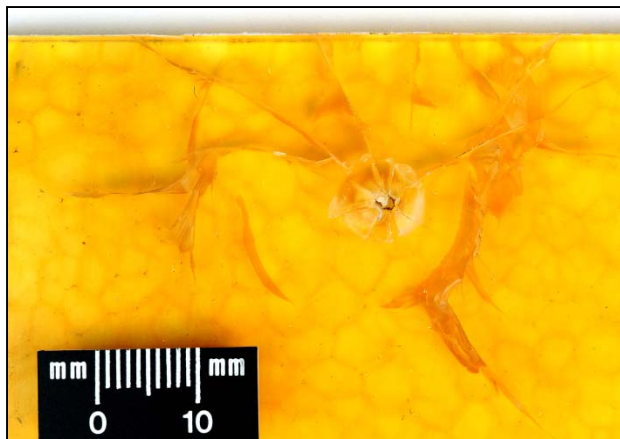


Front

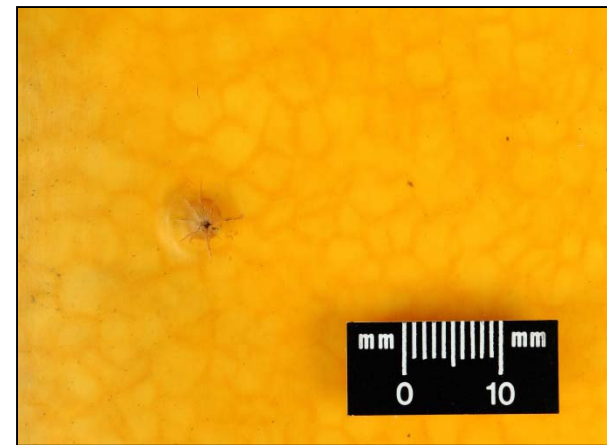


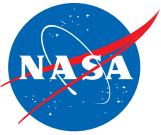
Test temperature: (25°C)

Test temperature: (50°C)



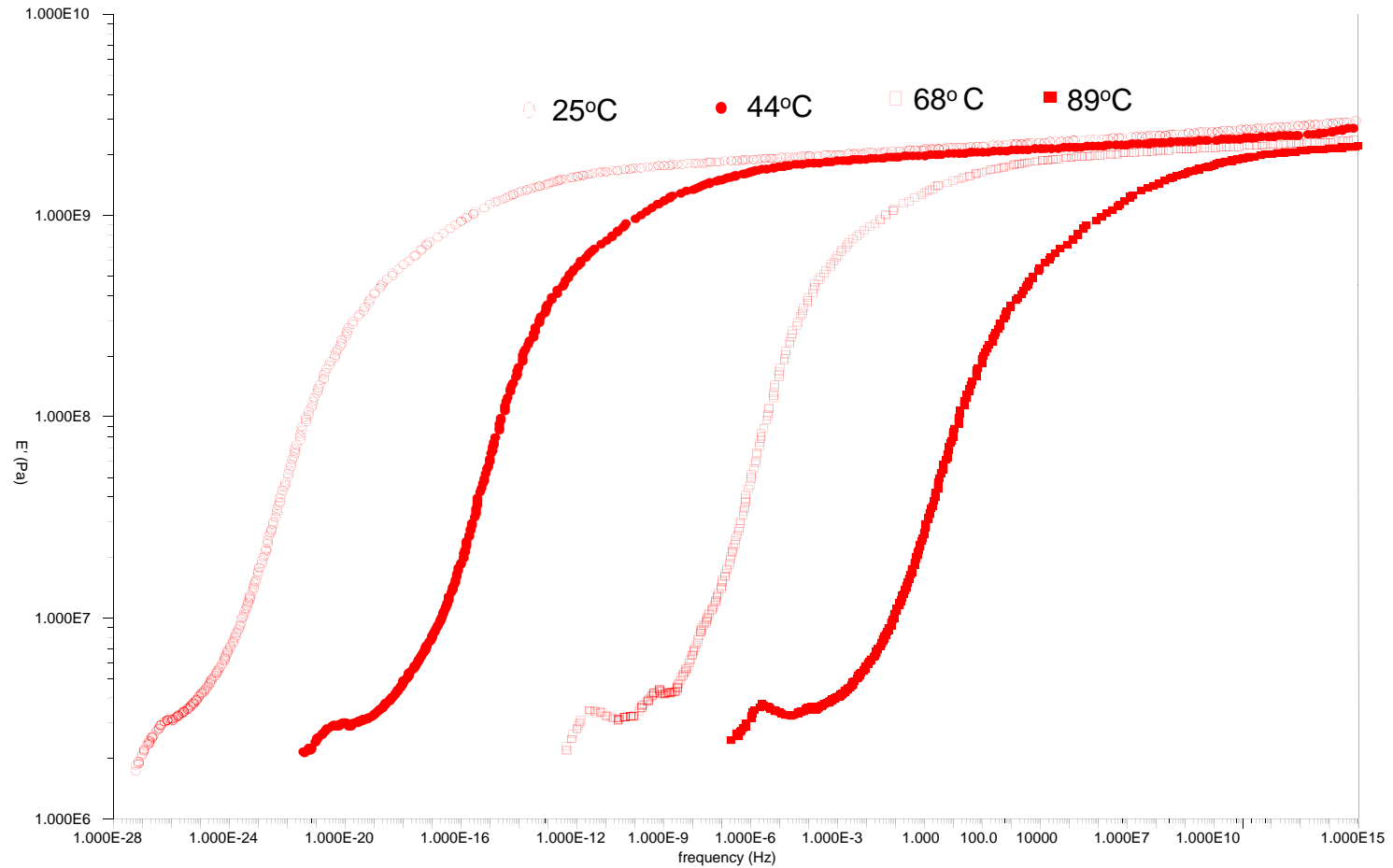
Back





Time Temperature Superposition Results

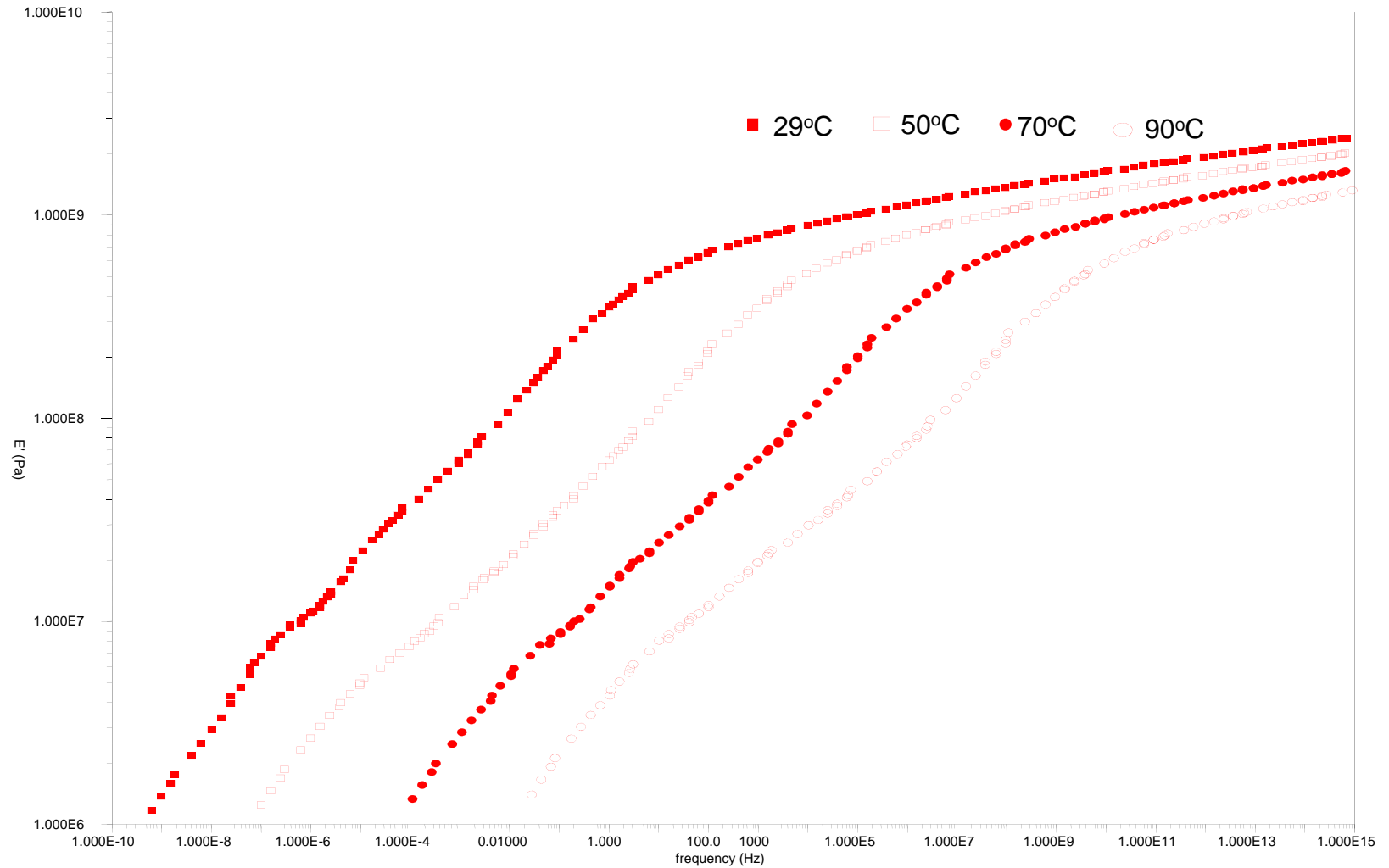
Master Curve - PB-g-PMA-co-PAN





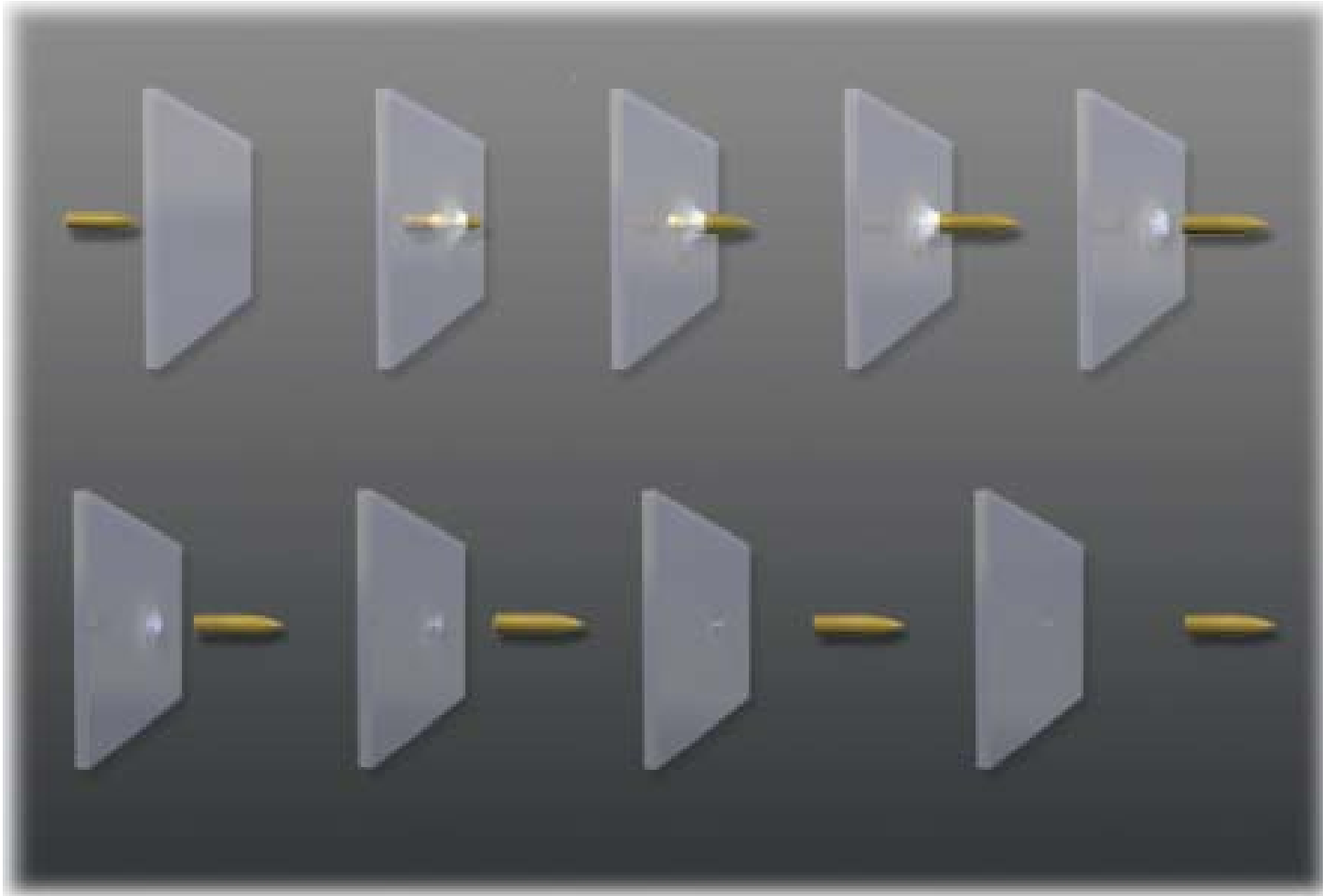
Time Temperature Superposition Results

Master Curve - Surlyn

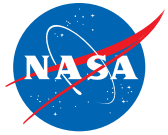




Puncture Self-Healing Mechanism



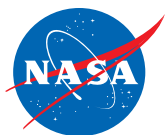
Bullet penetration schematic diagram of puncture healing mechanism



High Speed Video



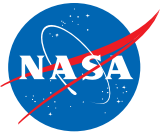
Surlyn



High Speed Video

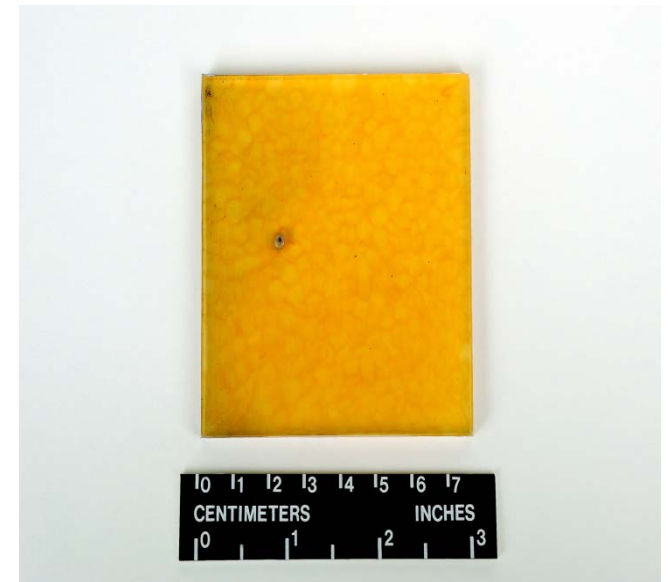


PB-g-PMA-co-PAN



Conclusions and Future Work

- Several commercially available polymers possessing unique puncture self-healing functionality at low to mid range temperatures have been identified.
- Puncture self-healing improved with increasing temperature for the commercially available polymer, PB-g-PMA-co-PAN.
- Puncture self-healing was more effective when site of impact temperatures were above glass transition temperatures and melting temperatures of respective polymers.
- High speed video confirmed puncture healing mechanism in Surlyn and PB-g-PMA-co-PAN.
- Incorporate computational methods in the design of new compositions.





Cross Cutting Applications

Fuel Tanks



Space Structures

